



## Selective recovery and separation of nickel and vanadium in sulfate media using mixtures of D2EHPA and Cyanex 272



Mehdi Noori<sup>a</sup>, Fereshteh Rashchi<sup>a,\*</sup>, Ataollah Babakhani<sup>a</sup>, Ehsan Vahidi<sup>b</sup>

<sup>a</sup> School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, PO Box 11155/4563, Tehran, Iran

<sup>b</sup> Ecological Sciences and Engineering Interdisciplinary Graduate Program, Purdue University, West Lafayette, IN 47907, United States

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### ABSTRACT

In this research, selective recovery and separation of nickel and vanadium in sulfate media was investigated by solvent extraction using D2EHPA, Cyanex 272, and their mixtures in various proportions. For this purpose, synthetic sulfate solutions of nickel and vanadium were prepared in 2 g/L of each metal. After dilution of the organic solvents in kerosene with the ratio of 1–4, experiments were carried out in the pH range of 1.0–7.0 in steps of 0.5 at ambient temperature. Solvent extraction of nickel and vanadium by sole D2EHPA was performed and the extraction percentages were determined to be 90% and 80% for nickel and vanadium, respectively. However, the co-extraction of nickel and vanadium by D2EHPA can be increased with increasing equilibrium pH and temperature. It was shown that using sole D2EHPA, pH<sub>50</sub> (the pH at 50% metal extraction) values for nickel and vanadium were 3.5 and 2, respectively; which is not appropriate for the efficient simultaneous separation of nickel and vanadium. Adding Cyanex 272 to D2EHPA in the organic phase, leads to a right shifting of extraction isotherm of nickel and a slight left shifting of the extraction isotherm of vanadium; thus, improves the separation of nickel over vanadium. To optimize the recovery and separation process of nickel and vanadium from the sulfate leach liquor, the influence of different D2EHPA to Cyanex 272 ratios and various temperatures (25, 35, 45, and 55 °C) were studied. As a result, optimum separation of vanadium over nickel was achieved with a Cyanex 272 to D2EHPA ratio of 0.35 M: 0.25 M. Based on the optimum results, pH<sub>50</sub> values for nickel and vanadium were shifted from 3.5 to 4.75 and from 2 to 1.75, respectively.

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### 1. Introduction

Due to the wide applications of vanadium and nickel in the steel industry as alloying elements, ceaseless extraction of mineral resources of these two metals are becoming more and more insufficient to answer the rapid growing demands especially in industrialized countries. On the other hand, fulfilling of burned or spent materials which contains toxic metals could leave irreparable environmental effects. In recent years, various secondary sources of vanadium and nickel such as fly ashes, crude oil, power plants residues, spent catalysts and stone coals have drawn attention of researchers to recovery of metals [1–4].

Fly ash generated by power plants is categorized as a special waste by US EPA. There are variety of fly ashes such as Cyclone Fly ash (CF) which is collected by cyclone collectors and Electrostatic Precipitated fly ash (EP) which is captured by electrostatic

collectors. These residues from fossil fuel combustion are captured by pollution control equipment and disposed in special landfills. The mentioned fly ashes are very fine and due to their low density, proper disposal of them is very difficult [5,6].

In landfills, leaching of heavy metals such as nickel and vanadium into ground water, soil, and/or surface water is the main potential environmental concern. Additionally, due to the limited storage capacity of landfills, safe disposal becomes more and more costly. Based on the statistics, the annual production of fly ash from coal-fired power plants (CFP) in Europe is almost 38 million tons. Furthermore, incinerators generate about 12 million tons of fly ash annually from 250 million tons of municipal solid wastes in Europe [7]. In Taiwan, the approximate production of fly ashes is 43,000 tons per year that 13,000 tons of total amount is EP fly ash and the rest is CY fly ash [6]. Also, The fraction of vanadium-containing fuel oil in power generation plant production at domestic thermal power stations in Russia is 13%; this corresponds to around 7 million tons per year [8]. Therefore, it is imperative to develop means of both diverting these types of wastes from the solid waste stream, and also recovering nickel and vanadium as

\* Corresponding author. Tel.: +98 21 88012999; fax: +98 21 88006076.

E-mail address: [rashchi@ut.ac.ir](mailto:rashchi@ut.ac.ir) (F. Rashchi).

valuable metals from fly ashes due to environmental and economic reasons.

Hence, in order to find a comprehensive route for extracting and separating nickel and vanadium, researchers have paid special attention to this subject in recent years. Different hydrometallurgical processes (leaching, ion exchange, electrolysis, cementation, precipitation, crystallization, and solvent extraction) have been used to recover and separate metals from each other [9]. Solvent extraction as one of the environmentally friendliest processes, is a hydrometallurgical method for purification, concentration, and separation of metals from each other [10,11]. Solvent extraction of nickel and vanadium was studied by using D2EHPA, Cyanex 272, Cyanex 923, Cyanex 302, and PC88-A as a synergist system or sole extractant for evaluating the separation and extraction of the metals in chloride and sulfate media [12–26].

In order to extract nickel and vanadium from secondary sources different hydrometallurgical routes have been used by researchers. Kersch et al. [7] studied extraction of heavy metals from fly ash by supercritical  $\text{CO}_2$  fluid and solvent extraction. Amer [27] leached boiler-ash with sulfuric acid to recover vanadium and nickel. Lai et al. [28] studied metals (e.g., Al, Co, Cu, Fe, Mo, Pb, V, and Zn) recovery from spent Hydro Desulfurization Catalysts (HDS) by electrolysis experiments. To recover Ni and V, acidic leaching of power plant fly ash which contains Ni, V, Mn, Fe, Cr, Mg, Zn, Pb, and Al was performed by Nazari et al. [29]. Except for nickel, vanadium and iron, concentration of other elements in the fly ash was less than 1%; therefore, the mentioned elements made no major influences on solvent extraction process. In addition, since  $\text{Fe}^{2+}$  is not extractable by D2EHPA and Cyanex 272 [19,30], to control iron concentration during the solvent extraction process, iron can be reduced from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In order to extract nickel and vanadium from heavy oil fly ash, Tokuyama et al. [31] investigated a process with two different steps; leaching and ion exchange. Al-Ghouti et al. [32] studied extraction and separation of vanadium and nickel from fly ash produced in heavy fuel plants. Although researchers have tried to develop a process for extracting and

separating both nickel and vanadium from secondary sources, they ended up with problems such as being time-consuming, contaminating ground water, producing degraded salts, operating non-selective, and not being cost-effective. On the other hand, some of the suggested routes only work out for vanadium; although, there were considerable amount of nickel or vice versa [1,5,33–35].

Instead of using a single extractant, mixtures of extractants can give rise to synergistic effects and better selectivity of metal extraction/separation in solvent extraction processes [16–22,36–38]. Previously, synergism has been applied to the separation of nickel–cobalt system by Darvishi and his co-workers. Using D2EHPA, Cyanex 272 and Cyanex 302, Babakhani et al. also studied synergism for separating nickel and cadmium from sulfate media by using mixtures of D2EHPA and Cyanex 302 [22]. In order to separate valuable metals such as cobalt, copper, manganese, and lithium from leach liquors of lithium ion batteries, mixtures of PC-88A and Cyanex 272 and their synergistic effects have been studied [39,40]. Also, influence of TBP as both an organophosphorus extractant [19,41–44] and a modifier [22,45] on solvent extraction systems has been investigated by various researchers. It is worth mentioning that TBP as a modifier could avoid the third phase formation and enhance separation factor during solvent extraction processes.

In the present study, solvent extraction has been used for extraction and separation of vanadium and nickel from sulfate solution. As a commercial extractant, D2EHPA has been used for extracting nickel and vanadium, despite the fact that D2EHPA has a co-extraction property [16,19,22,24,25,46]. Therefore, using sole D2EHPA is unacceptable for this purpose. Among cationic extractants Cyanex 272 shows better features of extraction on V (IV) and nickel (II) in sulfate medium while Cyanex 923 and 921 are suitable for chloride medium [14,16,25,46,47]. In addition, Cyanex 302 completed extraction of vanadium (IV) at pH 5 and Cyanex 301 extracts nickel and vanadium at nearly same pHs [48,49]. Although Cyanex 272 offers proper extraction and separation for both nickel and vanadium, it is relatively more expensive to be used commercially. Thus, for the commercial application aims,

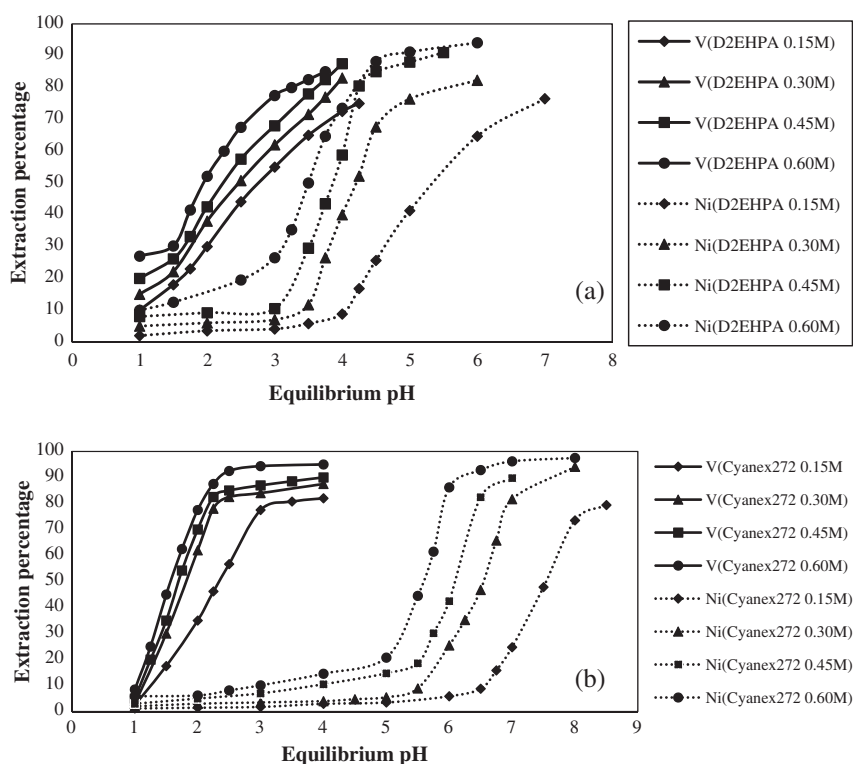


Fig. 1. Extraction of vanadium and nickel as a function of pH at 25 °C and O/A ratio of 1:1 in kerosene, (b) Cyanex 272.

effect of mixtures of D2EHPA and Cyanex 272 as synergistic extractants on the separation of nickel and vanadium was studied and discussed. In this regard, synergistic enhancement coefficient,  $R$ , as a parameter for considering effect of synergism and separation factor as a parameter for evaluating separation efficiency were studied. Finally, effect of temperature, TBP as a modifier, and thermodynamic aspect of the solvent extraction process were studied.

## 2. Experimental

### 2.1. Materials

Vanadyl sulfate (96% pure) and nickel sulfate (99% pure) salts were obtained from Merck, Germany. The organic solvents used

in this work were industrial-grade without further purification. Di-(2-ethylhexyl) phosphoric acid (D2EHPA), 97% pure, was purchased from Bayer, Germany and di(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), 90% pure, was supplied from Fluka, Canada. Kerosene, obtained from Tehran Oil Refinery Co., was used as diluent. Tri-*n*-butyl phosphate (TBP), 99% pure, purchased from Fluka, Canada was used as a modifier. Sulfuric acid (98% pure) and ammonium hydroxide, from Merck, Germany, were used as pH modifiers.

### 2.2. Experimental procedure

Stock solution of nickel (II) and vanadium (IV) with a concentration of 2 g/L from each metal ion was prepared by dissolving the required amount of nickel sulfate and vanadium sulfate in diluted

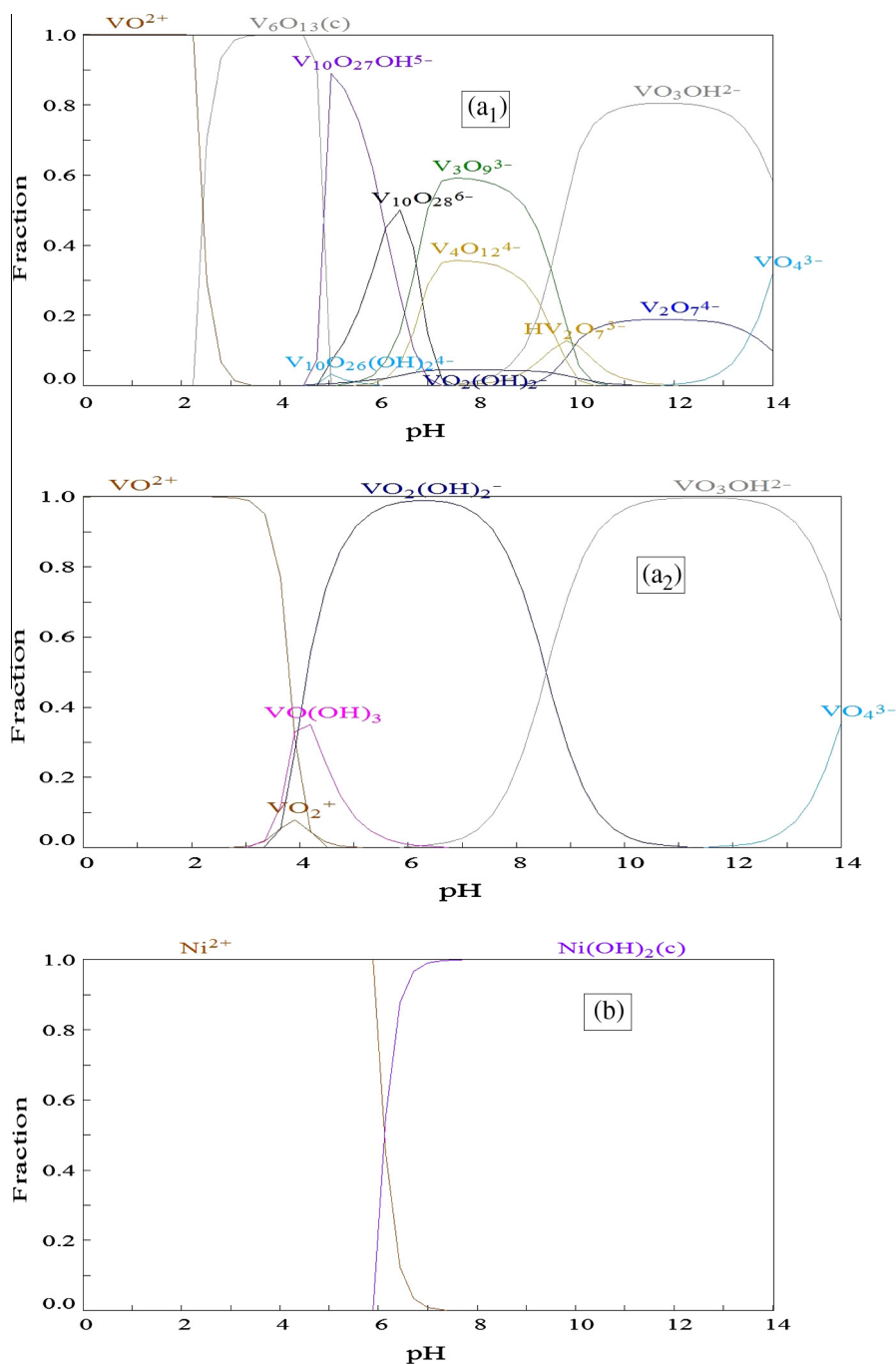


Fig. 2. Species distribution diagram of (a<sub>1</sub>) 40 mM vanadium at 25 °C and (a<sub>2</sub>) 1 μM vanadium at 25 °C and (b) 34 mM Nickel at 25 °C.

sulfuric acid solution with distilled water. The mentioned concentration is similar to the leachate solution of a typical fly ash feed. Each solvent extraction test was performed by mixing 200 mL of the aqueous phase solution with 200 mL of the organic phase containing 20% v/v of the extractant and 80% v/v kerosene. In extraction tests for plotting McCabe–Thiele diagrams,  $O/A$  ratio varied from 1:4 to 4:1. The concentration of the extractant in the organic phase (sole D2EHPA, Cyanex 272 or D2EHPA–Cyanex 272 mixtures) was 0.6 M in all experiments. Temperature of the system was controlled by a thermostatic bath and the extraction experiments were carried out at 25, 35, 45 and 55 °C. In order to obtain the extraction isotherms, pH was successively changed by adding either sulfuric acid (4 M) or ammonium hydroxide solution at 25% concentration drop wise; while the two-phase mixture was being agitated via a mechanical shaker. A PY-11 pH meter Sartorius made in Germany was used to monitor pH during the experiments and after the pH was stable, the mixture was agitated for at least 10 min to ensure that the equilibrium was attained. Then, a sample was taken, transferred to a separatory funnel, and allowed to disengage. In order to ensure the complete separation, a Hettich EBA-20 centrifuge was used by 5 min in 5000 rpm.

Nickel content was determined by complexometric titration using EDTA and murexide as indicator, and vanadium content determined by ferrous ammonium sulfate titration method [50]. Then, the concentration of metal ions in the organic phase was calculated from the difference between concentrations in the aqueous phase before and after extraction by mass balance [22,37].

The distribution ratio ( $D$ ) was calculated as the ratio of concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From  $D$  values, the percentage extraction ( $\%E$ ) and separation factor ( $\beta$ ) were calculated from:

$$\%E = \frac{D \times 100}{D + (V_{aq}/V_{org})} \quad (1)$$

where  $V_{aq}$  and  $V_{org}$  are the volume of aqueous and organic phase:

$$\beta = \frac{D_V}{D_{Ni}} = \frac{[V]_{org}/[V]_{aq}}{[Ni]_{org}/[Ni]_{aq}} \quad (2)$$

### 3. Results and discussion

#### 3.1. Effect of equilibrium pH

Fig. 1a shows the extraction percentage of vanadium and nickel ions as a function of equilibrium pH by using different concentrations of D2EHPA in kerosene at 25 °C and  $O/A$  1:1. As seen from extraction isotherms, by decreasing concentration of D2EHPA, extraction percentage of both metal ions from aqueous phase decreased at constant pH. It can also be concluded that increasing pH from 1 to 7 leads to an increase in extraction of both vanadium and nickel by D2EHPA as the extractant. In addition, the extraction isotherms are shifted to the right by decreasing D2EHPA concentration.

It can be seen in Fig. 1b, similar to the previous figure, with reducing concentration of Cyanex 272, extraction is completed at higher pHs. This variation in  $pH_{0.5}$  is more perceptive for nickel than vanadium and as depicted in Fig. 1b,  $pH_{0.5}$  of nickel varied from 5.6 to 7.6 by decreasing Cyanex 272 concentration from 0.6 M to 0.15 M. The possible variation of  $pH_{0.5}$  for vanadium and nickel could be explained by depicting species distribution diagrams.

Fig. 2a<sub>1</sub> illustrates the species distribution diagram of vanadium at concentration of 40 mM (2 g/L) at 25 °C. According to the figure, it is obvious that the only vanadium specie to be extracted by an anionic extractant, in this case, is  $VO^{2+}$  which is stable from pH 0

to 4 and obviously the concentration of the desirable specie is maximum up to pH 2. Fig. 2a<sub>1</sub> and c show that below pH ca. 3,  $VO^{2+}$  is the dominant vanadium species and Fig. 1b illustrates that at pH below ca. 2.3 vanadium extraction is maximum. At pH above 2.3, according to the species distribution diagram at 40 mM, the concentration of  $VO^{2+}$  reduces. However, based on the results in Fig. 1b it can be seen that the vanadium extraction is still maximum. This could be due to the fact that most of the vanadium in solution has been extracted before this pH and only about 5% is remained in aqueous phase. As shown in Fig. 2a<sub>2</sub>, distribution diagram for vanadium at 1  $\mu$ M concentration,  $VO^{2+}$  is dominant in a wider pH range (below pH 4). It is worth mentioning that as the extraction proceeds, most of the vanadium ions transfer to the organic phase; in other words, the concentration of vanadium decreases. Therefore, the pH range at which  $VO^{2+}$  is predominant, increases, as shown in Fig. 2a<sub>2</sub>. This figure illustrates the species distribution diagram for vanadium at 1  $\mu$ M concentration, which could be the extreme low concentration. The other species of vanadium are in anionic form which could not be extracted by anionic extractants.

Fig. 2b shows the species distribution diagram of nickel for 34 mM (2 g/L) at 25 °C. As can be seen at pH 0 to 7,  $Ni^{2+}$  is the only stable specie of nickel; however, at alkaline pH range of 7–14  $Ni(OH)_2$  is stable. Therefore, the only practical extractant for extraction of nickel must be anionic and  $pH_{0.5}$  could be changed from 0 to 7. Additionally, by using the data of Fig. 2a<sub>1</sub> and b, it is

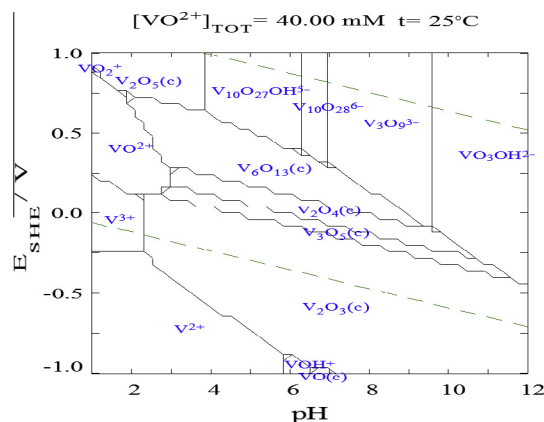


Fig. 3. The  $E_h$ -pH diagram of vanadium at 40 mM vanadium concentration at 25 °C.

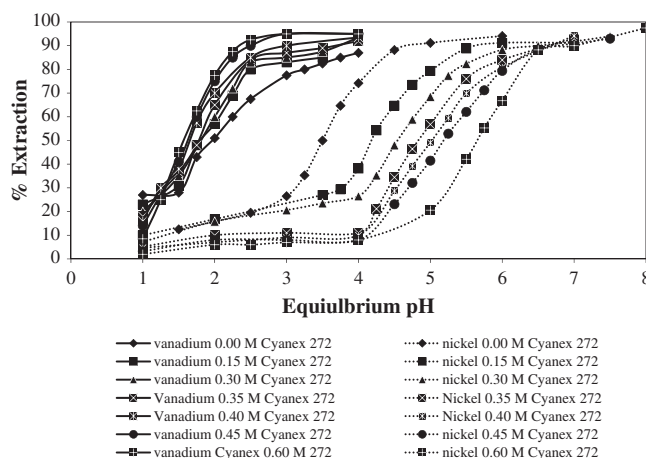


Fig. 4. Effect of increasing Cyanex 272 to D2EHPA on extracting nickel and vanadium at 25 °C and  $O/A$  ratio of 1:1 in kerosene.

obvious that changing of extractant and concentration of extractants could influence more on nickel than vanadium. The  $E_h$ -pH diagram for vanadium–water system at 25 °C is shown in Fig. 3. In aqueous solution, the colors of  $\text{VO}^{2+}$ ,  $\text{VO}_2^+$ ,  $\text{V}^{3+}$ ,  $\text{V}^{2+}$  are blue, yellow, green, and lilac, respectively [6,51]. Aqueous solution used in this study was blue which is an indication that  $\text{VO}^{2+}$  was the predominant species in the system. In addition, several investigations

emphasize that cationic extractants such as D2EHPA and Cyanex 272 extract vanadium as  $\text{VO}^{2+}$  from vanadium–water system [17,19,21,24,52].

Fig. 4 illustrates effect of adding Cyanex 272 to D2EHPA on the extraction and separation of vanadium and nickel ions as a function of pH at 25 °C. This figure demonstrates remarkable synergistic shifts of nickel isotherms to the right in the presence of Cyanex 272, but there are slight shifts to the left for vanadium isotherms. In other words, addition of Cyanex 272 to D2EHPA substantially improves the separation of  $\text{VO}^{2+}$  over  $\text{Ni}^{2+}$ .

As it can be seen from Table 1, the  $\Delta\text{pH}_{0.5}$  (difference between  $\text{pH}_{0.5}$  for vanadium and nickel) varied from 1.5 (for 0.6 M D2EHPA) to 4.1 (for 0.6 M Cyanex 272). Consequently, by using a mixture of Cyanex 272 and D2EHPA, value of the  $\Delta\text{pH}_{0.5}$  is higher than that of sole D2EHPA. Furthermore, Fig. 5 shows the synergistic effect of Cyanex 272 on  $\text{pH}_{0.5}$  and it can be seen that adding Cyanex 272 to D2EHPA relatively decreases  $\text{pH}_{0.5}$  values of vanadium and sharply increases those of nickel.

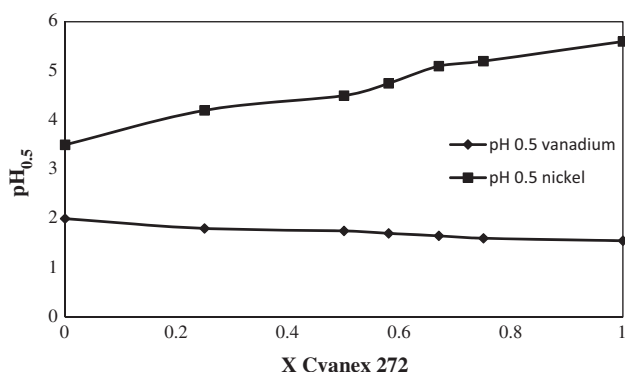
The distribution coefficient,  $D$ , was calculated as the concentration of metal ions in the organic phase to that part in the aqueous phase at equilibrium. The results of the distribution coefficient values and separation factor calculations are shown in Table 2. It is obvious that by increasing the Cyanex 272 to D2EHPA ratio separation factor increased. Although, at the first stages of adding Cyanex 272, a minor influence on separation factor was observed and after adding 0.3 M Cyanex 272 to D2EHPA, a significant influence started to occur as seen in Table 2. Maximum separation factor was obtained at pH 4 by sole Cyanex 272 ( $\beta = 219$ ). Since Cyanex 272 is more expensive than D2EHPA, solvent extraction process using sole Cyanex 272 is not cost-effective. Thus, the ratio of 0.25 M D2EHPA to 0.35 M Cyanex 272 was chosen as the best ratio under studied conditions.

In order to quantify the synergistic effect, the synergistic enhancement coefficient ( $R$ ) was defined as:  $R = D_{\text{mixture}} / (D_{\text{Cyanex272}} + D_{\text{D2EHPA}})$ , where  $D_{\text{mixture}}$ ,  $D_{\text{Cyanex272}}$  and  $D_{\text{D2EHPA}}$  are the distribution ratio of vanadium (or nickel) using the synergistic mixtures and the individual extractants, respectively [39,53,40,54]. Whatever the synergistic enhancement coefficient has more distance from 1, it means that addition of Cyanex 272 to D2EHPA has

**Table 1**

Values of  $\text{pH}_{0.5}$  for nickel and vanadium and  $\Delta\text{pH}_{0.5}$  (V–Ni) for different mixtures of D2EHPA and Cyanex 272 at 25 °C and O/A ratio of 1:1 in kerosene.

D2EHPA: Cyanex272	$\text{pH}_{0.5}$		$\Delta\text{pH}_{0.5}$ (V–Ni)
	V	Ni	
0.6:0.0	2	3.5	1.5
0.45:0.15	1.9	4.1	2.2
0.3:0.3	1.8	4.5	2.7
0.25:0.35	1.8	4.7	2.9
0.2:0.4	1.7	5.1	3.4
0.15:0.45	1.6	5.2	3.7
0.0:0.6	1.5	5.6	4.1



**Fig. 5.** Effect of adding Cyanex 272 on  $\text{pH}_{0.5}$  at 25 °C, and O/A ratio of 1:1 in kerosene.

**Table 2**

Values of  $D_V$ ,  $D_{Ni}$  and  $\beta_{V/Ni}$  for different mixtures of D2EHPA with Cyanex 272 at 25 °C, and O/A ratio of 1:1 in kerosene.

Molar ratio of D2EHPA: Cyanex 272	pH				
		1	2	3	4
0.60:0.00	$D_V$	$3.70 \times 10^{-1}$	1.04	3.44	5.67
	$D_{Ni}$	$1.11 \times 10^{-1}$	$1.90 \times 10^{-1}$	$3.61 \times 10^{-1}$	2.77
	$\beta_{V/Ni}$	3.33	5.47	9.53	2.05
0.45:0.15	$D_V$	$2.99 \times 10^{-1}$	1.33	4.88	$1.23 \times 10^1$
	$D_{Ni}$	$9.29 \times 10^{-2}$	$2.02 \times 10^{-1}$	$3.33 \times 10^{-1}$	$6.18 \times 10^{-1}$
	$\beta_{V/Ni}$	3.22	6.58	$1.47 \times 10^1$	$1.91 \times 10^1$
0.30:0.30	$D_V$	$2.50 \times 10^{-1}$	1.50	5.67	$1.43 \times 10^1$
	$D_{Ni}$	$7.76 \times 10^{-2}$	$1.88 \times 10^{-1}$	$2.59 \times 10^{-1}$	$3.61 \times 10^{-1}$
	$\beta_{V/Ni}$	3.22	7.98	$2.19 \times 10^1$	$2.49 \times 10^1$
0.25:0.35	$D_V$	$2.20 \times 10^{-1}$	1.86	7.33	$1.33 \times 10^1$
	$D_{Ni}$	$5.49 \times 10^{-2}$	$1.11 \times 10^{-1}$	$1.24 \times 10^{-1}$	$1.24 \times 10^{-1}$
	$\beta_{V/Ni}$	4.01	$1.67 \times 10^1$	$5.91 \times 10^1$	$1.07 \times 10^2$
0.20:0.40	$D_V$	$1.90 \times 10^{-1}$	2.33	7.33	$1.37 \times 10^1$
	$D_{Ni}$	$4.93 \times 10^{-2}$	$7.53 \times 10^{-2}$	$9.89 \times 10^{-2}$	$1.11 \times 10^{-1}$
	$\beta_{V/Ni}$	3.85	$3.09 \times 10^1$	$7.41 \times 10^1$	$1.23 \times 10^2$
0.15:0.45	$D_V$	$1.63 \times 10^{-1}$	3.00	$1.33 \times 10^1$	$1.90 \times 10^1$
	$D_{Ni}$	$3.31 \times 10^{-2}$	$8.70 \times 10^{-2}$	$8.70 \times 10^{-2}$	$8.70 \times 10^{-2}$
	$\beta_{V/Ni}$	4.92	$3.45 \times 10^1$	$1.53 \times 10^2$	$2.19 \times 10^2$
0.00:0.60	$D_V$	$9.29 \times 10^{-2}$	3.44	$1.33 \times 10^1$	$1.90 \times 10^1$
	$D_{Ni}$	$2.04 \times 10^{-2}$	$6.38 \times 10^{-2}$	$7.53 \times 10^{-2}$	$8.70 \times 10^{-2}$
	$\beta_{V/Ni}$	4.55	$5.39 \times 10^1$	$1.77 \times 10^2$	$2.19 \times 10^2$



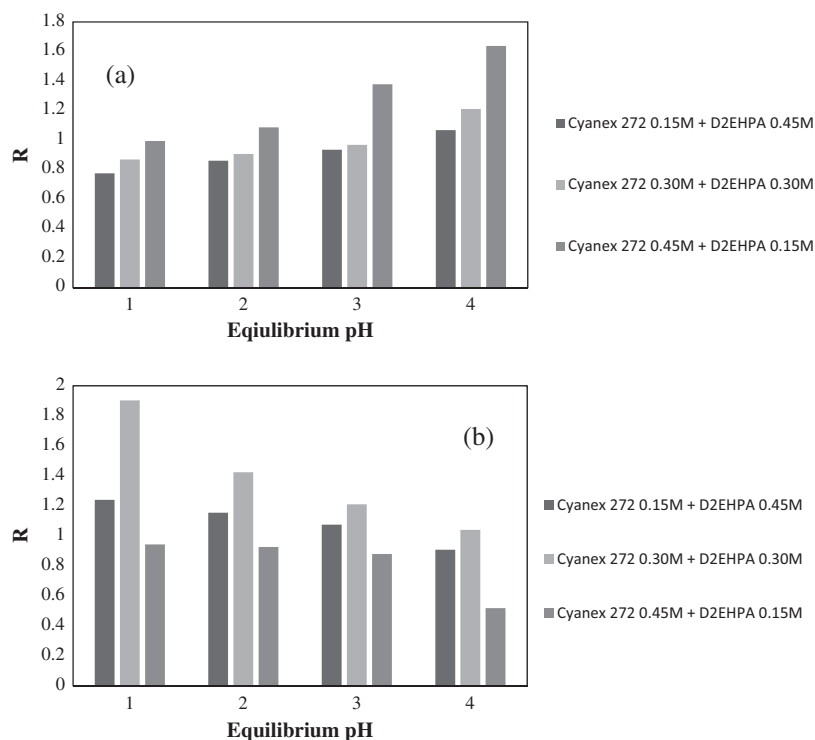


Fig. 6. Synergistic effect of adding Cyanex 272 to D2EHPA on, (a) vanadium synergistic enhancement coefficient ( $R$ ) and (b) nickel synergistic enhancement coefficient ( $R$ ).

more effect on nickel and vanadium extraction in comparison with using the mentioned extractants separately. The best condition will occur when the synergistic enhancement coefficient is greater than 1 and the maximum  $\Delta pH_{0.5}$  is obtained.

Fig. 6a and b demonstrate the synergistic effect of adding Cyanex 272 to D2EHPA on nickel and vanadium, respectively. According to Fig. 5a, at fixed pHs, with increasing concentration of Cyanex 272 to D2EHPA, it can be seen that synergistic coefficient increased. In other words, the mixture of extractants have positive effects on the extraction of vanadium than that of using each solely. At constant molar ratios of Cyanex 272 to D2EHPA, by increasing pH from 1 to 4 the synergistic coefficient increased to more than 1 which means adding Cyanex 272 to D2EHPA and increasing pH both enhance the extraction of vanadium. In case of nickel, at fixed pHs, by increasing Cyanex 272 to D2EHPA from molar ratios of 0.15:0.45 to 0.3:0.3 the synergistic enhancement coefficient is increased; however, at molar ratio of 0.15:0.45 D2EHPA to Cyanex 272 it is considerably decreased. At fixed molar ratios, by increasing pH from 1 to 4 the synergistic enhancement

coefficient strongly decreased to less than 1 which means adding Cyanex 272 to D2EHPA after 0.3:0.3 M ratio and varying pH from 1 to 4 both can reduce the extraction of nickel. To conclude, synergistic enhancement coefficient corresponds to a positive influence on vanadium extraction and in case of nickel makes a negative effect. However, the main aim of this study was separation of vanadium over nickel which was provided excellently by the mixture of Cyanex 272 and D2EHPA.

### 3.2. Influence of TBP concentration

To determine the effect of TBP as a modifier, experiments were carried out with 3% and 7% TBP in 0.25 M D2EHPA:0.35 M Cyanex 272 in kerosene at O:A ratio of 1:1 and temperature of 25 °C. Mixture of 0.25 M:0.35 M D2EHPA to Cyanex 272 was chosen because the selectivity of process from economical viewpoint is high enough. The addition of TBP caused the extraction isotherms of vanadium and nickel both to shift to the left which is shown by  $pH_{0.5}$  values for vanadium and nickel in Table 3. It reveals that

**Table 3**  
Values of  $pH_{0.5}$  for nickel and vanadium,  $\Delta pH_{0.5}$  (V–Ni), and separation factor at pHs 1–4 for different concentration of TBP at fixed concentration of 0.35 M Cyanex 272 to 0.25 M D2EHPA, O/A ratio of 1:1, and 25 °C in kerosene.

Parameters	TBP	pH	$pH_{0.5}$ (V)	$pH_{0.5}$ (Ni)	$\Delta pH_{0.5}$ (V–Ni)	$D$ (V)	$D$ (Ni)	SF
Values	0%	1	1.8	4.7	2.9	0.219	0.055	3.982
		2				1.857	0.111	16.730
		3				7.333	0.124	59.377
		4				13.286	0.136	97.691
	3%	1	1.6	4.4	2.8	0.299	0.022	13.907
		2				3.550	0.031	114.516
		3				12.889	0.099	130.324
		4				19.833	0.406	48.850
	7%	1	1.5	4.2	2.7	0.370	0.016	23.125
		2				9.000	0.020	441.176
		3				21.222	0.081	262.000
		4				30.250	0.572	52.885

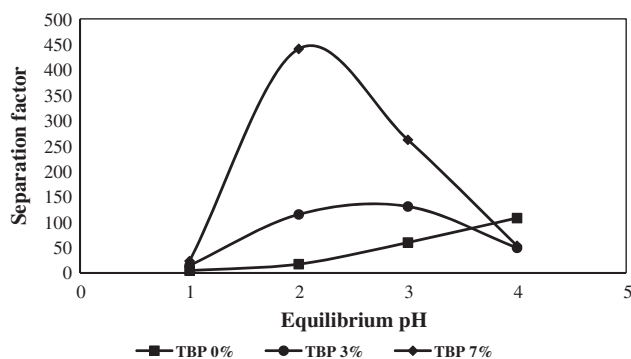


Fig. 7. Separation factor vs. equilibrium pH with TBP concentration: 0–7% at D2EHPA (0.25) M to Cyanex 272 (0.35 M), O/A ratio of 1:1, 25 °C in kerosene.

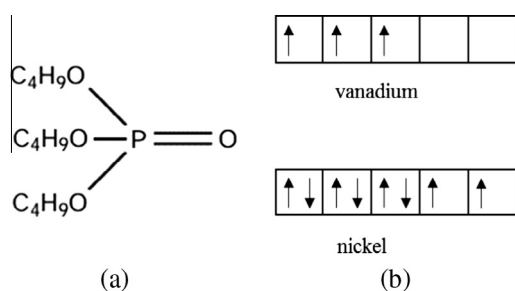


Fig. 8. (a) Structure of TBP, (b) schematic “d” orbitals of vanadium and nickel.

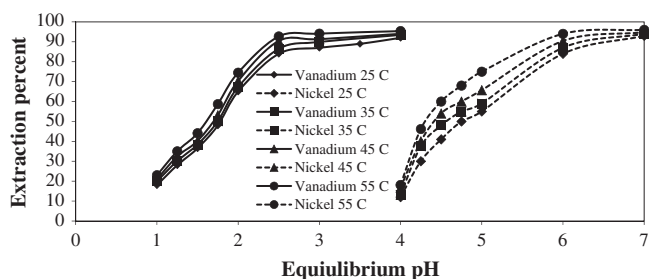


Fig. 9. Effect of temperature on the extraction of vanadium and nickel using 0.25 M D2EHPA and 0.35 M Cyanex 272 and A/O ratio of 1:1.

$\Delta\text{pH}_{0.5}$  of vanadium–nickel decreases from 2.9 (in the absence of TBP) to 2.7 (in the presence of 7% TBP). Fig. 7 shows the effect of TBP on separation factor. In this figure, it could be seen that by using 7% of TBP at pHs above 2 maximum separation factor (440) was achieved. Therefore, using 7% of TBP has a major positive influence on nickel and vanadium extraction, although it has a minor negative effect on  $\Delta\text{pH}_{0.5}$ .

It seems that TBP does not act through a synergistic process with D2EHPA and Cyanex 272. The fact is that addition of TBP at pH = 2 increased the extraction of vanadium over nickel in the system. This phenomenon could be attributed to the fact that atomic structure of vanadium and nickel are slightly different. As a transition metal, in both vanadium and nickel filling of the penultimate shell “d” orbitals occurs. However, in the case of vanadium with atomic number of 23 two vacant orbitals are available for bonding. These vacancies should be shared with the lone pair electrons of oxygen in TBP. Thus, complexes could be formed. As shown in Fig. 8 (added to the revised manuscript) in the case of nickel, all the “d” orbitals are filled or semi-filled with electrons. Therefore, nickel is not able to form complexes with TBP, i.e., being extracted to the organic phase.

### 3.3. Effect of temperature

To evaluate the effect of temperature, extraction isotherms of vanadium and nickel at 35, 45, and 55 °C were determined for a 0.35 M:0.25 M mixture of Cyanex 272:D2EHPA diluted in kerosene at O/A ratio of 1:1. These are shown in Fig. 9 alongside with the corresponding isotherms at 25 °C for comparison. Generally, the extraction of vanadium increases slightly as the temperature increases from 25 °C to 55 °C. Extraction of nickel also increases with increasing temperature from 25 to 55 °C. From Table 4 it can be seen that  $\Delta\text{pH}_{0.5}$  gradually increased. Thus, it can be concluded that both extraction isotherms are shifted to the left, but they are not to the same extent toward pHs by increasing the temperature. Extraction isotherm for nickel is shifted to the left more than vanadium. In conclusion, it indicates that higher temperatures are not beneficial for the separation of nickel and vanadium considering the amount of energy has to be consumed to elevate the temperature from 25 to 55 °C.

The influence of temperature has been studied in the present work for vanadium and nickel extraction at pHs 2 and 4.5, respectively at fixed concentrations of D2EHPA and Cyanex 272 (D2EHPA = 0.25 M, Cyanex 272 = 0.35 M) in a synergistic system. The relationship between distribution ratio and temperature is:

Table 4

Values of  $\text{pH}_{0.5}$  for nickel and vanadium and  $\Delta\text{pH}_{0.5}$  (V–Ni) for temperatures 25–55 °C, and separation factor for different pHs in O/A ratio of 1:1 in kerosene.

Parameters	Temp.	pH	$\text{pH}_{0.5}$ (V)	$\text{pH}_{0.5}$ (Ni)	$\Delta\text{pH}_{0.5}$ (V–Ni)	$D$ (V)	$D$ (Ni)	SF
Values	25 °C	1	1.8	4.7	2.9	0.219	0.055	3.982
		2				1.857	0.111	16.730
		3				7.333	0.124	59.377
		4				13.286	0.136	97.691
	35 °C	1	1.7	4.5	2.8	0.250	0.078	3.205
		2				2.058	0.133	15.474
		3				8.900	0.143	62.238
		4				14.385	0.152	94.630
	45 °C	1	1.6	4.3	2.7	0.266	0.093	2.860
		2				2.367	0.130	18.208
		3				10.494	0.170	61.729
		4				15.667	0.200	78.335
	55 °C	1	1.7	4.1	2.6	0.300	0.129	2.326
		2				2.921	0.165	17.703
		3				15.667	0.202	77.559
		4				20.739	0.227	91.361

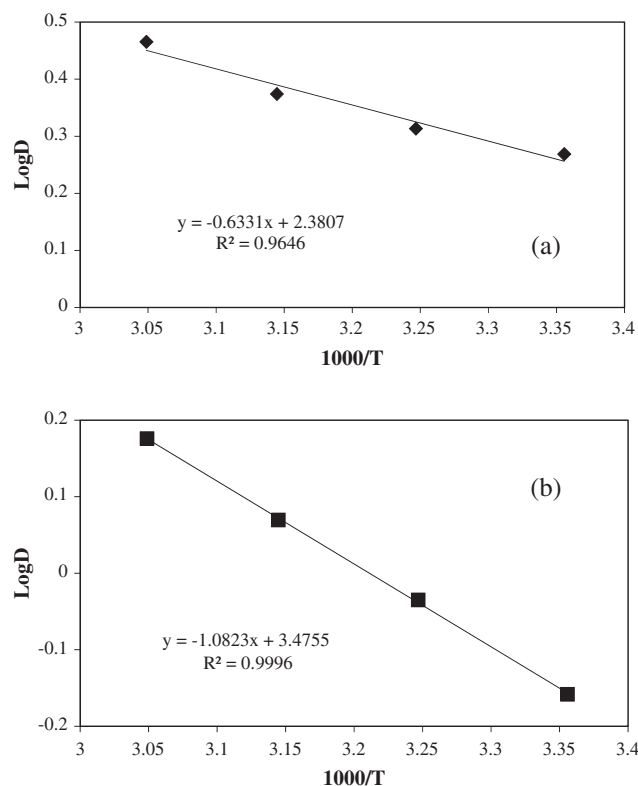


Fig. 10. Relationship between distribution coefficient and temperature for, (a) vanadium extraction, pH = 2 and (b) nickel extraction, pH = 4.

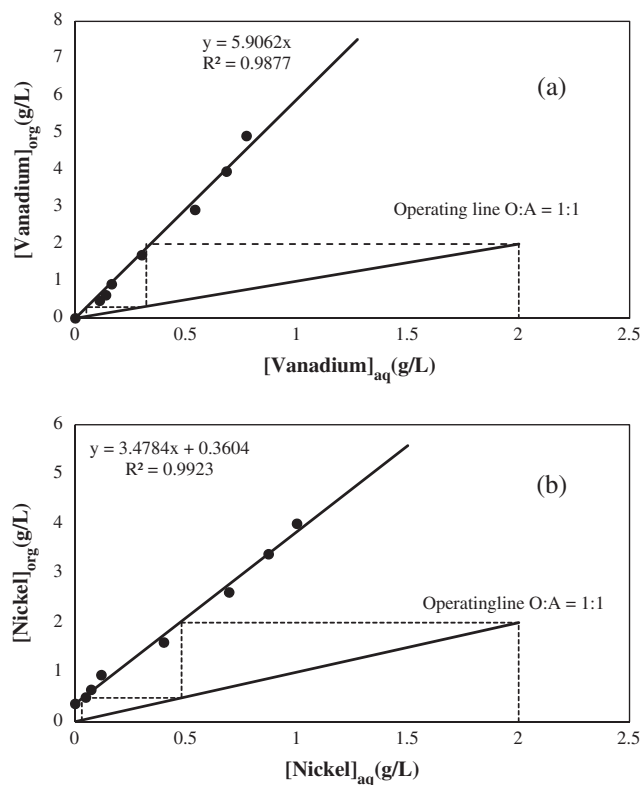


Fig. 11. McCabe–Thiele diagram at fixed concentration of D2EHPA (0.25 M) to Cyanex 272 (0.35 M) in kerosene, (a) for vanadium (IV) extraction and (b) for nickel (II) extraction.

$$\frac{\Delta \log D}{\Delta \left(\frac{1}{T}\right)} = \frac{-\Delta H}{2.303R} \quad (3)$$

By achieving distribution ratio and temperature, the change of enthalpy of the reaction,  $\Delta H$ , can be calculated. Plots of  $\log D$  versus  $T^{-1}$  ( $K^{-1}$ ) for vanadium and nickel are shown in Fig. 10 a and b, respectively. The  $\Delta H$  value was calculated for vanadium as  $12.12 \text{ kJ mol}^{-1}$  and also for nickel calculated as  $20.72 \text{ kJ mol}^{-1}$ . The sign of  $\Delta H$  for both metal ions are positive, indicating that the synergistic extraction process is endothermically driven. These results are comparable with the ones published by Li et al. [52] and Darvishi et al. [16].

#### 3.4. McCabe–Thiele diagram for extraction of nickel and vanadium

To determine the number of stages required at a selected volume phase ratio, vanadium (IV) and nickel (II) extraction isotherms at fixed concentration of D2EHPA 0.25 M to Cyanex 272 0.35 M were obtained at different O/A ratio from 1:4 to 4:1 at a pH of 2.5 for vanadium extraction and pH of 5.5 for nickel extraction, respectively. McCabe–Thiele diagrams of these metals are shown in Fig. 11 a and b. It was found that under the experimental conditions, vanadium (IV) (2 g/L) and nickel (II) (2 g/L) were completely extracted both in two stages.

#### 4. Conclusions

1. In extraction of vanadium and nickel from sulfate media, increasing Cyanex 272 to D2EHPA, at fixed total concentration of 0.6 M, caused a slight shift to the left on extraction isotherm of vanadium, but a major influence on nickel extraction by shifting the isotherm significantly to the right.
2. Maximum separation factor of 219 was obtained by using sole Cyanex 272.
3. Synergistic enhancement coefficient ( $R$ ) revealed that synergism has a positive effect on extraction of vanadium and negative effect on that of nickel.
4. Addition of TBP as a modifier has a major positive effect on separation factor, i.e., by using TBP (7%) at pH = 2 separation factor increased to 440.
5. Increasing temperature from 25 to 55 °C both nickel and vanadium extraction isotherms shifted to the left and no significant effect on the separation of both metals was observed.
6. Change of enthalpy,  $\Delta H$ , for vanadium and nickel was determined to be  $12.12 \text{ kJ mol}^{-1}$  and  $20.72 \text{ kJ mol}^{-1}$ , respectively.
7. McCabe–Thiele showed two stages of extraction for both nickel and vanadium at O:A = 1:1.

#### References

- [1] L. Zeng, Q. Li, L. Xiao, Extraction of vanadium from the leach solution of stone coal using ion exchange resin, *Hydrometallurgy* 97 (3–4) (2009) 194–197.
- [2] M.Y. Visaliev, M.Y. Shpirt, K.M. Kadiev, V.I. Dvorkin, E.E. Magomadov, S.N. Khadzhiyev, Integrated conversion of extra-heavy crude oil and petroleum residue with the recovery of vanadium, nickel, and molybdenum, *Solid Fuel Chem.* 46 (2) (2012) 100–107.
- [3] A. Ognyanova, A.T. Ozturk, I. De Michelis, F. Ferella, G. Taglieri, A. Akcil, F. Vegliò, Metal extraction from spent sulfuric acid catalyst through alkaline and acidic leaching, *Hydrometallurgy* 100 (1–2) (2009) 20–28.
- [4] R. Moskalyk, A. Alfantazi, Processing of vanadium: a review, *Miner. Eng.* 16 (9) (2003) 793–805.
- [5] S. Vitolo, M. Seggiani, S. Filippi, C. Brocchini, Recovery of vanadium from heavy oil and orimulsion fly ashes, *Hydrometallurgy* 57 (2) (2000) 141–149.
- [6] S. Tsai, M. Tsai, A study of the extraction of vanadium and nickel in oil-fired fly ash 22 (1998) 163–176.
- [7] C. Kersch, G.F. Woerlee, G.J. Witkamp, Supercritical fluid extraction of heavy metals from fly ash, *Ind. Eng. Chem. Res.* 43 (1) (2004) 190–196.



- [8] M.V. Tsygankova, V.I. Bukin, E.I. Lysakova, A.G. Smirnova, A.M. Reznik, The recovery of vanadium from ash obtained during the combustion of fuel oil at thermal power stations 52 (1) (2011) 19–23.
- [9] F. Habashi, A short history of hydrometallurgy, *Hydrometallurgy* 79 (1–2) (2005) 15–22.
- [10] T. Hosseini, F. Rashchi, E. Vahidi, N. Mostoufi, Investigating the synergistic effect of D2EHPA and Cyanex 302 on zinc and manganese separation, *Sep. Sci. Technol.* 45 (8) (2010) 1158–1164.
- [11] E. Vahidi, F. Rashchi, D. Moradkhani, Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA, *Miner. Eng.* 22 (2) (2009) 204–206.
- [12] V. Innocenzi, F. Veglio, Separation of manganese, zinc and nickel from leaching solution of nickel–metal hydride spent batteries by solvent extraction, *Hydrometallurgy* 129–130 (2012) 50–58.
- [13] T. Sato, Solvent extraction of vanadium (IV) from hydrochloridric acid solutions by neutral organophosphorus compounds, *Hydrometallurgy* 6 (1980) 13–23.
- [14] P.N. Remya, J. Saji, M.L.P. Reddy, Solvent extraction and separation of vanadium (V) from multivalent metal chloride solutions by Cyanex 923, *Solvent Extr. Ion Exch.* 21 (2007) 573–589.
- [15] N.I. Kasikova, A.G. Kasikov, V.T. Kalinnikov, Use of mixtures based on organophosphorous acids for the extraction of vanadium(IV) from model and industrial sulfurous solutions, *Theor. Found. Chem. Eng.* 43 (5) (2009) 816–821.
- [16] D. Darvishi, D.F. Haghsheenas, E.K. Alamdari, S.K. Sadrnezhaad, M. Halali, Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA, *Hydrometallurgy* 77 (3–4) (2005) 227–238.
- [17] L. Kurbatova, P. Slepukhin, D. Kurbatov, E. Zabolotskaya, Extraction of vanadium (IV) with DI-2-Ethylhexylphosphoric acid, *Phosphorus. Sulfur. Silicon Relat. Elem.* 187 (9) (2012) 1032–1037.
- [18] B.R. Reddy, D.N. Priya, K.H. Park, Separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquors of spent Ni–Cd batteries using phosphorus based extractants, *Sep. Purif. Technol.* 50 (2) (2006) 161–166.
- [19] X. Li, C. Wei, Z. Deng, M. Li, C. Li, G. Fan, Selective solvent extraction of vanadium over iron from a stone coal/black shale acid leach solution by D2EHPA/TBP, *Hydrometallurgy* 105 (3–4) (2011) 359–363.
- [20] A. Agrawal, P. Pathak, D. Mishra, K.K. Sahu, Solvent mediated interactions for the selective recovery of cadmium from Ni–Cd battery waste, *J. Mol. Liq.* 173 (2012) 77–84.
- [21] X. Li, C. Wei, J. Wu, M. Li, Z. Deng, C. Li, H. Xu, Co-extraction and selective stripping of vanadium (IV) and molybdenum (VI) from sulphuric acid solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, *Sep. Purif. Technol.* 86 (2012) 64–69.
- [22] A. Babakhani, F. Rashchi, A. Zakeri, E. Vahidi, Selective separation of nickel and cadmium from sulfate solutions of spent nickel–cadmium batteries using mixtures of D2EHPA and Cyanex 302, *J. Power Sources* 247 (2014) 127–133.
- [23] S. Jayadas, M.L. Reddy, Solvent extraction separation of vanadium (V) from multivalent metal chloride solutions using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, *J. Chem. Technol. Biotechnol.* 77 (10) (2002) 1149–1156.
- [24] Z. Cai, Y. Feng, H. Li, Y. Zhou, Selective separation and extraction of vanadium(IV) and manganese(II) from co-leaching solution of roasted stone coal and pyrolusite via solvent extraction, *Ind. Eng. Chem. Res.* 52 (38) (2013) 13768–13776.
- [25] M. Gharabaghi, M. Irannajad, A.R. Azadmehri, Separation of nickel and zinc ions in a synthetic acidic solution by solvent extraction using D2EHPA and Cyanex 272 49 (1) (2013) 233–242.
- [26] L.E.O.C. Rodrigues, M.B. Mansur, Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel–metal–hydride batteries, *J. Power Sources* 195 (11) (2010) 3735–3741.
- [27] A.M. Amer, Processing of Egyptian boiler-ash for extraction of vanadium and nickel, *Waste Manage.* 22 (5) (2002) 515–520.
- [28] Y.-C. Lai, W.-J. Lee, K.-L. Huang, C.-M. Wu, Metal recovery from spent hydrosulfurization catalysts using a combined acid-leaching and electrolysis process, *J. Hazard. Mater.* 154 (1–3) (2008) 588–594.
- [29] E. Nazari, F. Rashchi, M. Saba, in: 52nd Conference Of Metallurgists (COM), Optimum condition of vanadium recovery from power plant fly-ash with considering nickel behavior during the acidic leaching process using orthogonal array design, 2013.
- [30] M.R. Tavakoli, D.B. Dreisinger, Separation of vanadium from iron by solvent extraction using acidic and neutral organophosphorus extractants, *Hydrometallurgy* 141 (2014) 17–23.
- [31] H. Tokuyama, S. Nii, F. Kawaizumi, K. Takahashi, Process development for recovery of vanadium and nickel from heavy oil fly ash by leaching and ion exchange, *Sep. Sci. Technol.* 38 (6) (2003) 1329–1344.
- [32] M.a. Al-Ghouti, Y.S. Al-Degs, A. Ghrair, H. Khoury, M. Ziedan, Extraction and separation of vanadium and nickel from fly ash produced in heavy fuel power plants, *Chem. Eng. J.* 173 (1) (2011) 191–197.
- [33] P. Taylor, E. Guibal, J. Guzman, R. Navarro, J. Revilla, Vanadium extraction from fly ash – preliminary study of leaching, solvent extraction, and sorption on Chitosan, *Sep. Sci. Technol.* 38 (12–13) (2003) 37–41.
- [34] S. Vitolo, M. Seggiani, F. Falaschi, Recovery of vanadium from a previously burned heavy oil fly ash, *Hydrometallurgy* 62 (3) (2001) 145–150.
- [35] R. Navarro, J. Guzman, Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes, *Waste Manage.* 27 (2007) 425–438.
- [36] M. Ahmadipour, F. Rashchi, B. Ghafarizadeh, N. Mostoufi, Synergistic effect of D2EHPA and Cyanex 272 on separation of zinc and manganese by solvent extraction, *Sep. Sci. Technol.* 46 (15) (2011) 2305–2312.
- [37] T. Hosseini, N. Mostoufi, M. Daneshpayeh, F. Rashchi, Hydrometallurgy modeling and optimization of synergistic effect of Cyanex 302 and D2EHPA on separation of zinc and manganese 105 (2011) 277–283.
- [38] E. Vahidi, M. Noori, F. Rashchi, A. Babakhani, Solvent extraction and separation of nickel and vanadium from sulfate leach liquor of power plant fly ash using D2EHPA and Cyanex 272, *AIChE Annual Meeting*, 2013.
- [39] F. Wang, F. He, J. Zhao, N. Sui, L. Xu, H. Liu, Extraction and separation of cobalt(II), copper(II) and manganese(II) by Cyanex272, PC-88A and their mixtures, *Sep. Purif. Technol.* 93 (2012) 8–14.
- [40] J.M. Zhao, X.Y. Shen, F.L. Deng, F.C. Wang, Y. Wu, H.Z. Liu, Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A, *Sep. Purif. Technol.* 78 (3) (2011) 345–351.
- [41] D. Haghsheenas Fatmehsari, D. Darvishi, S. Etemadi, A.R. Eivazi, E. Keshavarz Alamdari, a.a. Salardini, Interaction between TBP and D2EHPA during Zn \* Cd \* Mn \* Cu \* Co and Ni solvent extraction: a thermodynamic and empirical approach, *Hydrometallurgy* 98 (1–2) (2009) 143–147.
- [42] Z. Zhu, W. Zhang, Y. Pranolo, C.Y. Cheng, Separation and recovery of copper, nickel, cobalt and zinc in chloride solutions by synergistic solvent extraction, *Hydrometallurgy* 127–128 (2012) 1–7.
- [43] P. Narayanan Remya, M. Lakshminpathy Reddy, Solvent extraction separation of titanium (IV), vanadium (V) and iron (III) from simulated waste chloride liquors of titanium minerals processing industry by the trialkylphosphine oxide Cyanex 923, *J. Chem. Technol. Biotechnol.* 79 (7) (2004) 734–741.
- [44] J. Thomas, G.D. Surender, M.L.P. Reddy, Solvent extraction separation of vanadium (V) from multimetal chloride solutions using tributylphosphate, *Sep. Sci. Technol.* 38 (15) (2003) 3761–3774.
- [45] C.Y. Cheng, Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime, *Hydrometallurgy* 84 (1–2) (2006) 109–117.
- [46] M.K. Nazemi, F. Rashchi, Recovery of nickel from spent NiO/Al<sub>2</sub>O<sub>3</sub> catalyst through sulfuric acid leaching, precipitation and solvent extraction, *Waste Manage. Res.* 30 (5) (2012) 492–497.
- [47] L. Zeng, C.Y. Cheng, A literature review of the recovery of molybdenum and vanadium from spent hydrosulphurisation catalysts, *Hydrometallurgy* 98 (1–2) (2009) 1–9.
- [48] R.K. Biswas, A.K. Karmakar, Equilibrium of the extraction of V (IV) in the V(IV)-SO<sub>4</sub><sup>2-</sup>(H<sup>+</sup>, Na<sup>+</sup>)–Cyanex 302–Kerosene system, *Int. J. Nonfer. Metal* 1 (3) (2012) 23–31.
- [49] R.K. Biswas, A.K. Karmakar, Liquid–liquid extraction of V (IV) from sulphate medium by Cyanex 301 dissolved in kerosene 2 (1) (2013) 21–29.
- [50] A.I. Vogel, Quantitative Inorganic Analysis, John Wiley and Sons, New York, 1989.
- [51] G. Bauer, Vanadium and vanadium compounds, *Ullmann's Encyclopedia Ind. Chem.* (2000).
- [52] X. Li, C. Wei, J. Wu, C. Li, M. Li, Z. Deng, H. Xu, Thermodynamics and mechanism of vanadium(IV) extraction from sulphate medium with D2EHPA, EHEHPA and CYANEX 272 in kerosene, *Trans. Nonferrous Met. Soc. China* 22 (2) (2012) 461–466.
- [53] Y. Pranolo, W. Zhang, C.Y. Cheng, Recovery of metals from spent lithium-ion battery leach solutions with a mixed solvent extractant system, *Hydrometallurgy* 102 (1–4) (2010) 37–42.
- [54] Z. Zhang, H. Li, F. Guo, S. Meng, D. Li, Synergistic extraction and recovery of cerium (IV) and Fluorin from sulfuric solutions with Cyanex 923 and di-2-ethylhexyl phosphoric acid, *Sep. Purif. Technol.* 63 (2) (2008) 348–352.